

REMOTE X-RAY DIFFRACTION AND X-RAY FLUORESCENCE ANALYSIS ON PLANETARY SURFACES

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ABSTRACT

The legacy of planetary X-ray Diffraction (XRD) and X-ray Fluorescence (XRF) began in 1960 when W. Parish proposed an XRD instrument for deployment on the moon. The instrument was built and flight qualified, but the Lunar XRD program was cancelled shortly before the first human landing in 1969. XRF chemical data have been collected *in situ* by surface landers on Mars (Viking 1 & 2, Pathfinder) and Venus (Venera 13 & 14). These highly successful experiments provide critical constraints on our current understanding of surface processes and planetary evolution. However, the mineralogy, which is more critical to planetary surface science than simple chemical analysis, will remain unknown or will at best be imprecisely constrained until X-ray diffraction (XRD) data are collected. Recent progress in X-ray detector technology allows the consideration of simultaneous XRD (mineralogic analysis) and high-precision XRF (elemental analysis) in systems miniaturized to the point where they can be mounted on fixed landers or small robotic rovers. There is a variety of potential targets for XRD/XRF equipped landers within the solar system, the most compelling of which are the poles of the moon, the southern highlands of Mars and Europa.

REMOTE SENSING OF SOLAR SYSTEM OBJECTS

Remote spectral analysis techniques have been applied to many objects within our solar system, with the result that in general terms, we know the compositions of the solid surfaces that we can image. In some instances, high-resolution spectral data are available as is the case for the Moon, Mars, and Europa, among others. However, even these high-resolution images and analyses have lateral spatial resolutions of tens to thousands of meters, orders of magnitude larger than the scale length of the phases (e.g., minerals) which comprise the images. The elemental / chemical information obtained by remote sensing, while informative, has spawned a cottage industry of studies of analog materials and a myriad of interpretations. Remote sensing is principally useful in the formulation of hypotheses that can later be investigated by *in-situ* analysis techniques.

There is a wide variety of objects in our solar system to which *in-situ* instrument packages could be profitably deployed:

- The rocky planets Mercury, Venus and Mars,
- Rocky planetesimals, including asteroids and planetary moons,
- Icy planetesimals, including Kuiper belt objects, Oort cloud comets and icy moons

What would we like to learn by studying these objects?

- *Origin of the Solar System.* Asteroids and comets have crystallization ages which predate the formation of the planets. An understanding of their mode of formation will shed light on early solar nebula processes and planet formation.
- *Comparative planetology.* By analyzing planetary materials from Mars, Venus and Earth, information on early differentiation, plate tectonics, upper mantle and crustal processes, the presence/absence of magnetic fields over time can be determined and compared.
- *Natural history of volatiles, biogenic elements.* Water and other volatiles, including the entire inventory of the biogenic elements H, C, O, N, S and P may have been deposited onto the surfaces of the rocky planets as a thin veneer during the late bombardment of the early solar system. What is the source of the volatiles? What is their distribution over space and time?
- *Did life evolve there?* Earth harbors the only example of life as we know it, but we have reason to believe that life could originate wherever appropriate conditions exist (liquid water, a source of simple carbon-containing molecules and energy). Such conditions apparently existed on Mars in the distant past, and perhaps in the water ocean thought to exist below the ice-covered surface of Europa.
- *Can we live there?* Human missions to Mars are being planned, perhaps as early as 2018. Permanent colonization will require utilization of local resources for food and shelter.

Much of this information is contained in the mineralogy of planetary surfaces. We have learned a great deal from remote sensing techniques, but real answers, particularly where mineralogy is involved, will require *in-situ* instruments, and it is argued, X-ray diffraction / X-ray fluorescence analysis.

IN-SITU MINERALOGICAL ANALYSIS OF PLANETARY SURFACES

One of the most informative characteristics of a planetary surface is its mineralogy. Suites of surface minerals can be used to characterize past and present climatic conditions, sedimentary weathering processes or hydrothermal activity. More than elemental data, mineralogical data are linked to surficial conditions and processes and can be used to elucidate present and past conditions of the atmosphere, the surface, the crust, and occasionally the deep interior of a planet. Minerals have known ranges of stability and paragenetic relationships. Even when minerals persist out of their stability fields (as is common in sedimentary rocks), disequilibrium associations, or the presence of relict unstable phases, can be used to unravel detailed sedimentary or diagenetic histories which can themselves be linked to climate history.

However, despite the power of mineralogy as a descriptive and diagnostic tool for planetary exploration, the most powerful of the mineralogical methods, X-ray diffraction, has not been used to date on planetary missions. Diffraction methods are distinct from all other techniques that characterize minerals, in that diffraction data can be used to determine crystal structure (and mineralogy) directly and unequivocally without a requirement for ground truth data.

In this brief review, an historical perspective for planetary XRD/XRF will first be presented, by highlighting spacecraft instruments that have flown or that have been proposed for flight. Next, a modern landed planetary XRD/XRF instrument concept will be described. Lastly, planetary missions are described for which XRD/XRF could provide important answers.

X-ray instruments that have been developed/ flown

1968	Lunar XRD (not flown)
1972	Viking 1&2 XRF
1982	Venera 13 & 14 XRF
1997	Mars Pathfinder APX

HISTORICAL PERSPECTIVE OF XRD/XRF INSTRUMENTATION

The lunar XRD instrument¹

Between 1960 and 1968, considerable effort was expended in designing and building a practical XRD for use on the moon. The first proposal for a planetary XRD was from William Parrish of Philips Electronic Instruments in 1960. A series of breadboard and prototype instruments was constructed at JPL in the following years. The final flight prototypes, which were Bragg-Brentano geometry instruments utilizing a Cu X-ray tube, Soller slits and Xe gas proportional detectors, achieved a performance equal to laboratory diffractometers. The instruments suffered from relatively unreliable power supplies, and, at 20 kg, were heavy for spacecraft instruments. The lunar XRD program was ended in 1968 without ever deploying an instrument on a lunar mission (Dunne and Nickle 1968).

A number of prototype XRD instruments were built and evaluated during the years 1964-1968. Combined XRD/XRF instrument concepts were investigated as well, and it was concluded that such capabilities were feasible in a flight instrument using current-day technology. In addition to the basic instrumentation, simple drills and sample delivery devices were devised to provide powder samples to the instrument. The USGS utilized one of the prototype XRD instruments as a field-operable system, and performed hundreds of diffraction analyses during two field tests.

The Viking XRF instrument²

In early 1977, the two Viking landers began transmitting data from the surface of Mars. One of the most successful of the instruments aboard – the Viking XRF, began sending data on the elemental makeup of Mars surface soil. Both sites returned analyses of fine-grained samples that were very similar – Si and Fe in large amounts and Mg, Al, Ca, and S in significant amounts. Modeling of the results suggested that the main components were SiO₂ (45%), Fe₂O₃ (18%), Al₂O₃ (5%), MgO (8%) CaO (5%) and SO₃ (8%).

The instrument utilized two radioactive sources, ⁵⁵Fe and ¹⁰⁹Cd, to produce X-rays with energies of 5.9 KeV, 22.2 KeV, and 87.7 KeV. Fluorescence of X-rays from all elements of the periodic

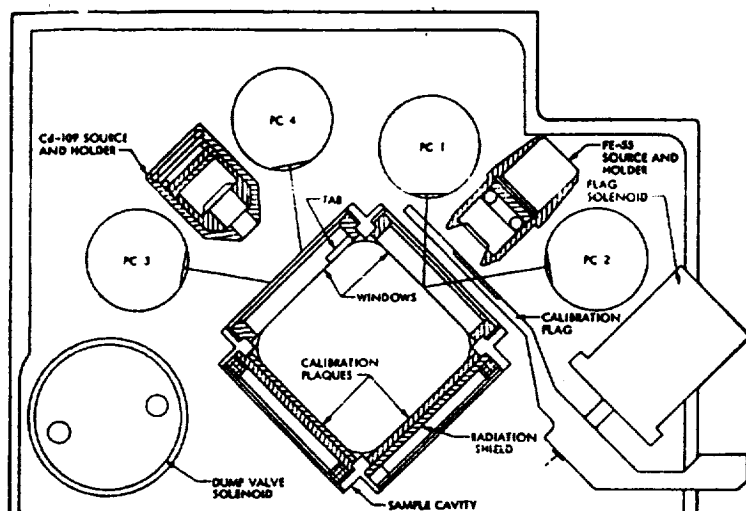


Figure 1. Analysis section of the Viking XRF. radioisotopic sources, proportional counter detectors and sample cavity are shown in plan view (after ref. 2).

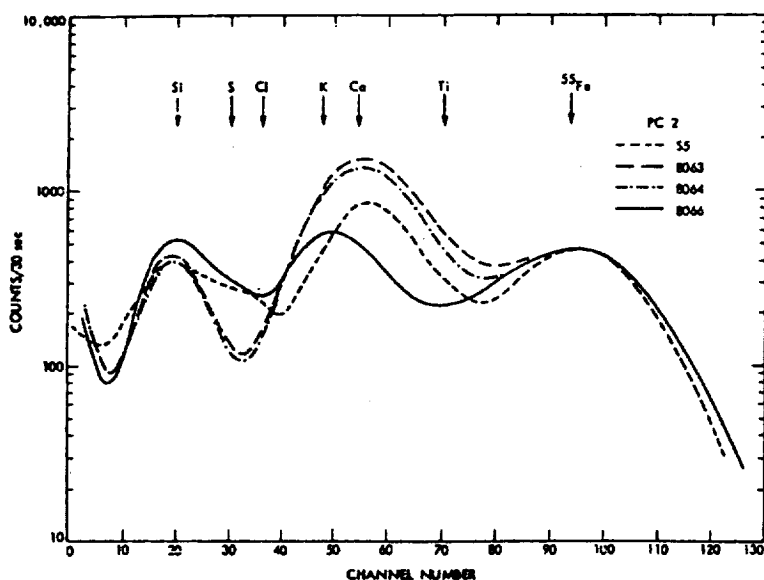


Figure 2. Comparison of Viking lander 1 spectrum from proportional counter #2 with three Earth standard materials, including igneous and sedimentary rocks (after ref. 2).

table was possible, although the nature of the detectors and detector windows limited the sensitivity only to elements above Na. While solid state energy-dispersive detectors were available at the time, the cooling requirements for these detectors made them unsuitable for the Viking XRF experiment. Rather, gas proportional counters were used which had much reduced resolution, but could operate at ambient temperature on the surface of Mars. Figure 1, a plan view of the analysis section of the XRF instrument, shows the radioisotope sources, proportional counter detectors and sample cavity. Fig. 2 shows one of the first soil analyses transmitted from the surface of Mars. The results of the Viking XRF experiment suggest that the surface "fines" analyzed by the instrument consist of iron-rich smectite clays, carbonates, iron oxides (maghemite?) and sulfate minerals concentrated in a duricrust.

In the succeeding 25 years, the Viking XRF results have not been challenged by any of the remote spectral techniques, and no reinterpretations of the data were made until the most recent pathfinder lander APXS analyses.

Venera 13 & 14

Between 1971 and 1982, the Soviet Union deployed a remarkable series of instruments to Venus, culminating in landers which relayed photographs of the Venusian surface and XRF analyses of the surface material. This was a remarkable accomplishment given the fact that the surface temperature of Venus is nearly 500° C and the surface pressure is 65 atmospheres of corrosive sulfur dioxide and sulfuric acid vapor.

Upon landing, the Venera landers deployed a drill to obtain surface materials that were transported inside the pressure hull of the lander. The analysis chamber was cooled to 30° C and evacuated to 0.05 bar. The sample was irradiated by ^{55}Fe and ^{238}Pu isotopic sources. Fluorescence X-rays were detected by gas proportional counters and classified utilizing a 256 channel pulse height analyzer. The Venera 14 lander survived 57 minutes, relaying data on composition which suggested that the soil of Venus is similar in composition to oceanic basalts on the Earth. Figure 3 shows a crosssection of the Venera lander in the vicinity of the analysis chamber. Figure 4 shows a spectrum of a Venusian rock analyzed by Venera 13, relative to spectra of alkaline basalts from the Earth.

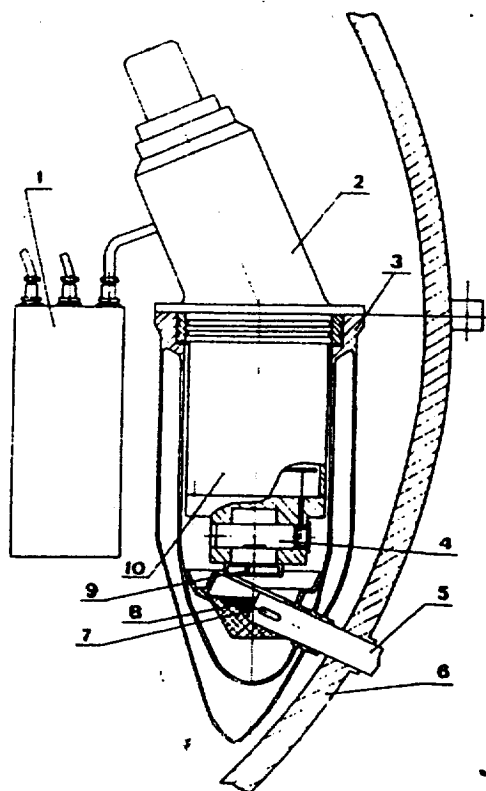


Figure 3. Design and position of the detection unit of the X-ray spectrometer on landing modules of Venera 13 and 14. (1). multichannel analyzer, (2). lid of the detection unit, (3). body of the detection unit, (4). counter, (5). air lock, (6). hull of the lander module, (7). sample being analyzed, (8). soil receiver, (9). radioisotopic source, and (10), electronics section. (after ref 3).

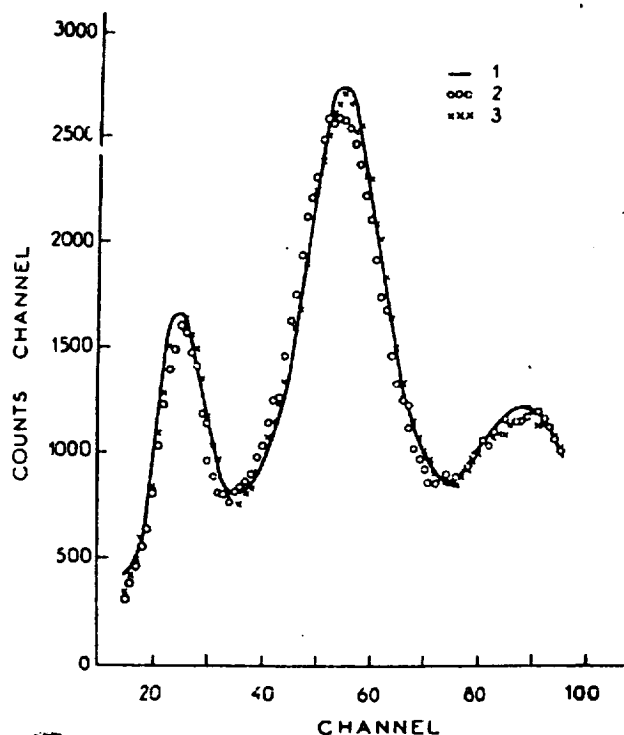


Figure 4. X-ray spectrum of Venusian rock measured by Venera 14 (1) and spectra of the Atlantic tholeiitic basalts of the Earth (2 and 3). (after ref. 3)

Mars pathfinder APX instrument⁴

The Mars pathfinder spacecraft landed on the surface of Mars on July 4, 1997 in what was principally intended as a technology demonstration of a novel landing system. A brief time later, the Sojourner rover rolled down the ramp of the lander and began to explore and measure its surroundings using multispectral imaging cameras and an Alpha Proton X-ray Spectrometer (APXS). In all, the APXS analyzed a dozen soil samples and rocks. The analyses proved difficult because all of the rocks were covered with loose soil or weathering rinds which interfered with the analyses.

In operation, the Alpha Proton X-ray Spectrometer (APXS) sensor head was placed against a rock or soil sample for a period of 10 hours. The sensor head contains a radioactive alpha particle source (curium) and three detectors: a telescope containing two silicon detectors, for alpha particles and protons, and a silicon-PIN X-ray detector and pre-amplifier. The particles interact with the sample in three ways. Elastically scattered alpha particles are picked up by the alpha particle detector. Protons from alpha-proton nuclear reactions are measured by the proton detector. X-ray fluorescence due to alpha particle bombardment yields information on the abundance of elements, Na and above. A combination of all three measurements allows determination of the abundance all elements except hydrogen at concentration levels above typically a fraction of one percent. Unfortunately, interferences with the Mars atmosphere caused the alpha backscatter and proton spectral measurements to be uninterpretable. The principal results of the APXS instrument on Pathfinder were due to XRF analysis. XRF analyses of rocks and soil from the Pathfinder landing site were more silica rich, on average than expected, suggesting that a significant amount of crustal differentiation or fractional crystallization of basaltic melts had taken place.

THE CHALLENGE AND PROMISE OF MODERN XRD/XRF INSTRUMENTATION

All of the landed planetary missions to date have determined composition or chemistry alone, without structural data. In this section an XRD/XRF instrument is described which is intended for use on remote planetary missions. The instrument, which is called CHEMIN for its ability to determine both CHEmistry and MINeralogy, can directly determine the mineralogy of soil and windblown dust, or of suitably prepared rock samples.⁵ CHEMIN will employ a low-power Cu X-ray tube. Collimated X-rays, comprised of bremsstrahlung and Cu characteristic radiation, penetrate a thin powder sample. Forward-scattered diffracted X-ray photons and fluorescent X-rays characteristic of the sample are collected and recorded by a 2-dimensional charge-coupled device (CCD) detector (Fig. 5). The detector intersects diffraction angles from 2° to 60° 2θ (d -values of $\sim 17\text{\AA} - 2\text{\AA}$), a range that includes definitive diffraction peaks for virtually all minerals as well as maxima for amorphous materials. The detector is an energy discriminating CCD which is directly exposed to the X-ray flux exiting the sample. The CCD will be passively cooled in the environment of the Martian surface to $<230\text{ K}$ to reduce dark current and its associated noise. An XRD pattern is recorded as a 2-D image comprised of all pixels which have collected a charge equivalent to a primary beam X-ray photon (Fig. 6). An XRF analysis of the sample is obtained by summing all X-ray photons into a multichannel analyzer (Fig. 7). With a suitable CCD, these X-rays provide an analysis of all elements $Z > 5$ in the sample.

The addition of a diffraction-based instrument to the suite of instruments available for planetary missions will allow, for the first time, the direct determination of the mineralogy of planetary surfaces.

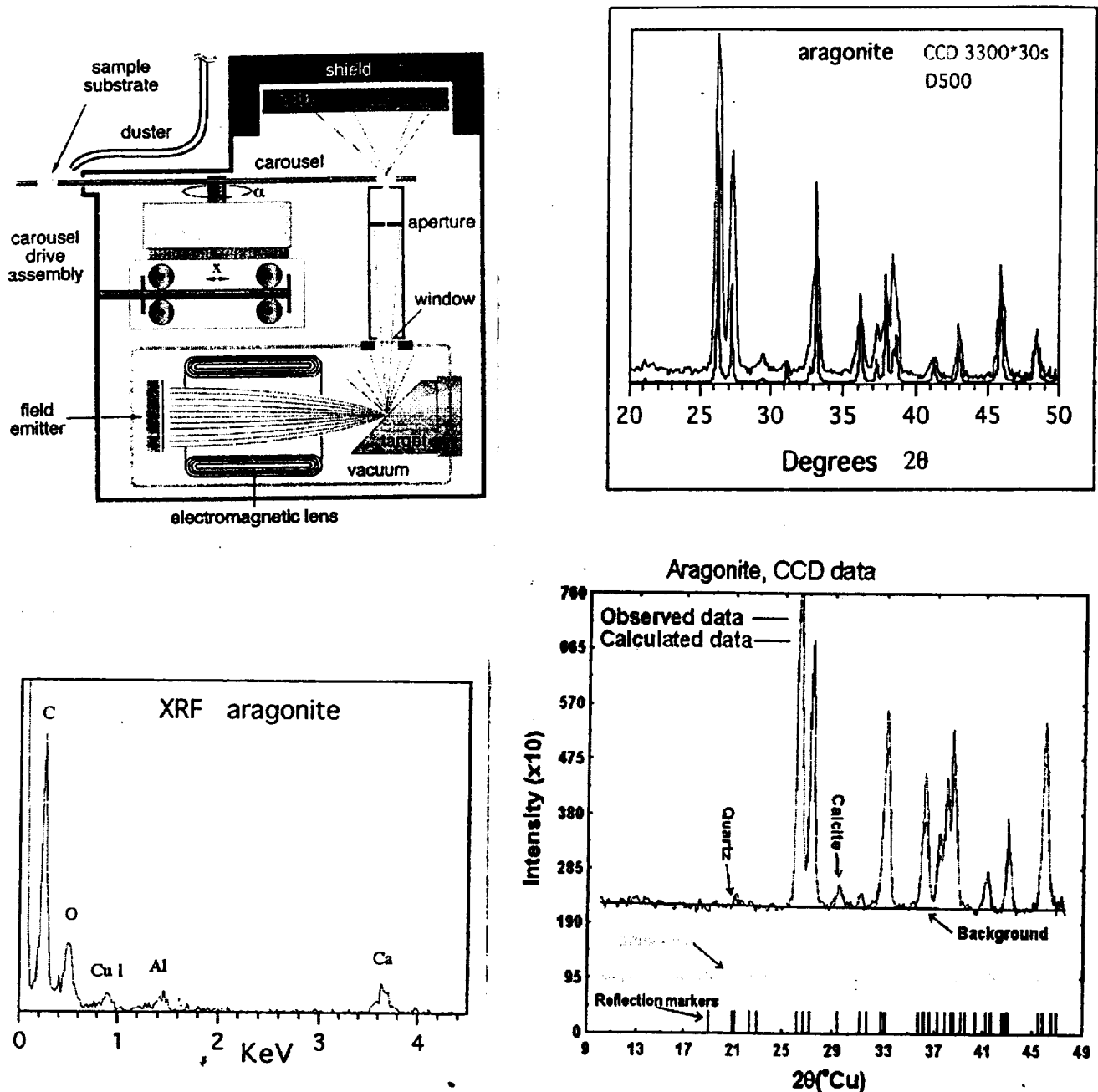


Figure 5. Cross-section of proposed CHEMIN flight instrument. Powder samples are supported on thin film sample holders which are rotated from the sample collection position into the analysis position. Transmitted diffraction and fluorescence photons are detected by an energy-discriminating CCD. Figure 6. Diffraction pattern of Aragonite from CHEMIN prototype, compared with laboratory data. Figure 7. X-ray Fluorescence spectrum of aragonite, recorded utilizing a CHEMIN breadboard instrument, Al and Cu are from the sample holder and X-ray tube. Figure 8. Rietveld refinement of CHEMIN prototype diffraction data from aragonite.

WHAT'S NEXT: PROPOSALS FOR DEPLOYMENT OF XRD/XRF SYSTEMS

1. The moon

The Earth's moon has been visited by us a number of times, and during the Apollo program, several hundred kilograms of rocks and soil were returned to the Earth for analysis. However, it may be surprising to learn that we are still very much interested in returning to that body to analyze additional materials. The Gamma Ray Spectrometer on the Lunar Prospector mission identified excess hydrogen within craters at the poles of the Moon, thought to be water about 40 cm beneath the surface in perennially shaded regions.⁶ This water is in all likelihood a vestige of the late bombardment of the inner solar system by icy planetesimals. The water is presumably from the same outer solar system reservoir of icy objects that must have bombarded the Earth, and we would like to know whether the Earth's oceans are indeed a legacy of cometary influx. This original hypothesis – that the world's oceans and other volatiles were delivered to a barren and rocky, volatile-free early Earth, has been challenged by recent remote analyses of a number of cometary bodies which suggest that cometary water is too high in deuterium to have contributed significantly to the ocean. The nature of the water reservoir at the lunar poles is uncertain. The Lunar Prospector fast and epithermal neutron data indicate as much as 40 cm of desiccated regolith above water-ice reservoirs in permanently shadowed polar craters. It is unlikely that this reservoir is a simple accumulation of ice within regolith pore space. Limited data on the lunar geotherm (four measurements from the Apollo missions) indicate temperatures of ~245-255 K at regolith depths of 40 cm, well below the freezing temperature for pure water ice but within a range where brines may exist as liquids.

These factors indicate that any surface exploration of the lunar poles for water should be provided with (1) an ability to drill to depths of >40 cm and (2) the capability to determine the mineral and chemical constituents of the samples obtained. The samples obtained by such a system could be readily analyzed by XRD/XRF. X-ray diffraction analysis, coupled with X-ray fluorescence can explicitly determine not only the presence of hydrous alteration phases such as clays or zeolites, but can also identify the structural variants or types of clay or zeolite present (e.g., well-ordered versus poorly-ordered smectite; chabazite versus phillipsite). In addition, XRF can readily measure the abundances of key elements that may occur in lunar zeolites (Na, Mg, Al, Si, K, Ca, Fe) as well as the likely constituents of lunar brines (F, Cl, S). Finally, if coring and analysis is performed during the lunar night, XRD can provide information on any crystalline ices that might occur in the regolith samples. Beyond an abiding scientific interest in the presence of water and its source, the identification of a significant source of water on the moon virtually guarantees the success of a lunar colony.

2. Mars

Mars is the only planet in our solar system that could have sustained life as we know it early in solar system history, and therefore occupies a special place in solar system exploration. The importance of Mars to our exploration activities is illustrated by the fact that NASA is planning two missions to Mars, an orbiter and a lander, at each launch opportunity (about every two years). The principal emphasis of this robotic exploration initiative is first, to ascertain whether

life ever existed on Mars, and second, to pave the way towards human exploration in the early-to-mid 21st century.

The Importance of Mineralogical Analysis to Mars Paleoclimatology and the Exobiological exploration of Mars

Mineralogical analysis, by which it is meant the determination of both crystal structure and elemental composition, could lend insight into the early history of Martian volatiles, could establish the presence and lateral extent of hydrothermal systems, and could reveal the locations of rock types (silica sinter, travertine, etc.) which may harbor evidence of liquid water, prebiotic organic material or even extinct life. Once mineralogical surveys are completed, follow-on studies could perform *in situ* mineralogical analyses of rock outcrops or select the most likely candidate rock samples for return to Earth. Categories of Paleoclimatological / Exobiological research interest are listed below along with a description of their distinctive mineralogical characteristics.

The early history of Martian volatiles

Mars is presently a dry eolian planet with a tenuous atmosphere of ~7 millibar, dominated by CO₂. However, ancient surface morphological features such as stream channels and other fluvial and lacustrine features provide compelling evidence that liquid water existed on the surface of Mars in large quantity. This apparent abundance of liquid water implies that early Mars was once wetter and warmer, and had a dense atmosphere. The total quantity of water which apparently existed on the surface of Mars early in its history cannot be accounted for by the polar caps alone. In addition to that water lost to space, it is likely that hydrated phases exist either as a consequence of their direct deposition from aqueous solution or as products of the reaction of anhydrous igneous minerals with water. The quantity, type and degree of crystallinity of clays, micas and other hydrated phases can be determined by mineralogical analysis and their known stability relationships can constrain the conditions under which they formed.

The presence and lateral extent of hydrothermal systems

Abundant morphological evidence exists for early and extensive volcanic activity on the surface of Mars, and for the presence of liquid water. The juxtaposition of these features is compelling evidence that hydrothermal systems once (or have always) existed on Mars. Ancient hydrothermal systems could have been eroded or exhumed, exposing minerals and mineral assemblages at the surface which were formed at depths inaccessible in presently active systems. The mineralogical characterization of such a system would provide an evaluation of the role hydrothermal processing has played in modifying the early Martian atmosphere and in altering deep-seated igneous rocks.

Evidence of prebiotic organic chemistry:

On the Earth, all evidence of prebiotic organic chemistry has been erased. In the earliest terrestrial rocks for which conditions of formation and of subsequent metamorphism would permit it,

evidence of life is present. Therefore, even if life never originated on Mars, it would be exceedingly valuable to find some evidence in the geologic record of Martian prebiotic organic chemistry. This would be possible on Mars more than on the Earth since, due to the apparent absence of large-scale plate tectonics, extensive regions of ancient terrain exist on Mars that have not been subject to metamorphism. Current concepts of prebiotic organic chemistry suggest that many important reactions have occurred in hydrothermal systems where some energy could have been provided by mineral hydration reactions. Hydrothermal systems also provide a means for gas exchange with the atmosphere and transport of reactants to the sites of reactions. Once hydrothermal terrains are identified by their distinctive mineralogy, areas or samples can be chosen for more comprehensive organic analyses or sample return.

Evidence of extinct Life

Evidence of life on the Earth occurs in the earliest rocks which could have preserved signs of its presence ~3.5 billion years ago. However, much of the geologic record from the earliest sedimentary sequences has either been heated to the extent that metamorphism would have removed evidence of life, or has simply been destroyed by burial and subduction. Because of the apparent lack of plate-tectonic activity on Mars, a great deal of the sediment deposited on the ancient Martian surface probably still exists and was probably not heated to as high a temperature as equivalent age sediments on the early Earth. Impact heating could still have obliterated ancient surface material, but orbital mapping should be able to identify old, undisturbed sediments. Therefore, it is likely that if life originated early in Martian history, some record of its existence would be manifest in the earliest geologic record which should be accessible to surface landers.

Absolute determination of the presence of prebiotic organic material or of evidence of extinct or extant life will most likely require the return of a sample to Earth. The purpose of *in-situ* sample analysis on the Martian surface would be to survey rocks or sediments, to ensure that the very best candidates for fossiliferous strata are collected, and to provide a global or regional context for the samples brought back.

SUMMARY AND CONCLUSIONS

A critical component of planetary surface exploration is mineralogical analysis. X-ray fluorescence chemical data have been collected *in-situ* by surface landers on Mars and Venus. These experiments have provided critical constraints on our current understanding of surface processes and evolution of these planets. Nevertheless, elemental data alone leave serious gaps in our understanding of the surfaces of planets where complex minerals may form in combination with H, S, and halogens. On such planets (e.g., Mars) a single elemental composition may represent a wide range of mineral assemblages. The mineralogy, which is more critical to planetary surface science than simple chemical analysis, will remain unknown or will at best be imprecisely constrained unless X-ray diffraction (XRD) data are collected. Several prototype XRD/XRF instruments are being built, and it is highly likely that X-ray diffraction analysis, proposed by Parrish nearly 40 years ago, will become a common method for planetary surface analysis in the not-so-distant future.

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